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The Weathering Study of PC/ASA Alloy For Automotive Exterior Applications

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Abstract: Polycarbonates (PC) are used in automotive industry due to their high physical and mechanical properties like high impact resistance and ductility. Polycarbonates are blended with ABS (Acrylonitrile-Butadiene-Styrene) and ASA (Acrylonitrile-Styrene-Acrylate) terpolymers for interior and exterior applications of automotive components to achieve good physical and mechanical properties. Other reason for choosing such alloys for interior applications is the IZOD impact resistance requirement higher than 40 kJ/m^2. Recently, grades of PC/ASA with UV stabilization are developed for non-painted exterior applications. The aim of our study is to investigate whether new developed PC/ASA could be chosen for exterior applications of automotive industry. In this study, the samples are prepared from injection molding and the weathering performance of PC/ASA was tested by a weather-o-meter for 1500 h at a total of 1890 kJ/m^2 at 340 nm with a cut-off filter at $\lambda<290$ nm. The results are evaluated by FT-IR, DSC, TGA, and SEM. It has been observed that UV degradation of PC/ASA leads to several major changes in its IR spectrum like broad bands occurring in the hydroxyl region around 3300 cm^{-1}, and carbonyl stretching region increased intensity around 1728 cm^{-1}. The main degradations were based on photo-oxidation and photo-Fries rearrangement of PC. In our study, the photo-oxidation was followed by the color shift to yellowing of the polymer.

Keywords: PC/ASA Alloy, weathering, photo-oxidative degradation, automotive exterior applications, thermoplastic.

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INTRODUCTION

It is possible to modify some properties of deficient polymers in a blend. When the polymers are compatible to be mix in a matrix, the resulting properties are studied for special applications. By controlling the formulation of the material, one can achieve a balanced property with synergistic effect. Polycarbonate (PC) has difficulties in production process due to high melt viscosity. PC has high modulus, high toughness and high impact strength and suitable to be used for blending with other polymers. In the literature, blending with a rubber-toughened thermoplastic Acrylonitrile-Butadiene-Styrene (ABS) has been investigated for observing the mechanical properties (1). Such studies on PC/ABS blends have confirmed that the poor chemical resistance and thermal stability are the main drawbacks of PC/ABS. The butadiene rubber in ABS undergoes chemical aging under UV radiation which decreases the mechanical properties and changes the color (2). ASA terpolymer where butadiene rubber in ABS is replaced with acrylic rubber solves the problem of butadiene degradation. In the case of PC and Styrene-Acrylonitrile (SAN) blends, compatibilizer is required to the blends of PC/ABS and PC/ASA for enhancing the interaction energy. PC and ABS are not totally miscible and requires polar groups and reactive functional polymers for decreasing the interfacial tension between phases (3). Especially for automotive applications where high toughness is required, the interfacial interaction is necessary for welding operations where poor adhesion at welding results into failure (4). Further studies with different compatibilizers were tested for increasing the mechanical properties (5). Such former studies have revealed that thermal and mechanical properties are improved by blending PC and ASA. On the contrary, the drawback of PC/ASA blend is the degradation of PC under UV radiation which is the main objective of this study. The effect of UV degradation on properties and morphology is described.

MATERIALS AND METHODS

Materials

The material used was Luran S KR2863 C (Ineos-Styrolution). (Vicat Method A: 150 °C, MFI 260 °C, 5 kg: 18 cm^3/10 min, HDT A 1.80 MPa: 109 °C, Izod Notched Method A 23 °C: 600 kJ/m^2) The material was injected molded as a complete part with the injection parameters requested by the material supplier. The specimen for UV radiation was prepared by cutting the complete part from the flat surface in dimensions of 65 mm x 140 mm where thickness was 4 mm.

Accelerated Weathering Test

The aging test was performed according to FIAT 50451 Standards for parts used in vehicle exterior which is used for understanding the behavior of the material under atmospheric agents like light, relative humidity, and temperature. The exposure time was up to 1500 hours. Atlas

Xenon test chamber was used with a black panel temperature of 65 °C ± 3 °C where the air in the chamber was 40 °C ± 3 °C. A Xenon lamp at 340 nm and 0.35 W/m^2 light intensity with $\lambda<290$ nm cut-off filter (borosilicate/borosilicate) was used. The total irradiation was 1890 kJ/m^2. The cycle parameters exposed to the samples were 18 minutes of humidifying and light, and 102 minutes of drying and light (the relative humidity during drying was 60%).

Characterization

FT-IR: The samples are measured by Bruker Tensor II within the range 4000 - 400 cm^{-1}. The spectrum was collected by a Diamond crystal attenuated total reflectance (ATR) module, using 24 sample scans and resolution of 4 cm^{-1}. The effect of aging on hydroxyl region, carbonyl groups and aromatic groups attached to carbonyl groups were observed.

Spectrophotometry: The samples are measured by benchtop spectrophotometer Datacolor 500 (Datacolor). The color measurements were performed by pulsed Xenon flash lamp in the range of 360-700 nm. The sample data was evaluated after obtaining L value (positive ΔL darkness, negative ΔL lightness), a value (positive means red, negative means green) and b value (positive means yellow, negative means blue).

TG/DTG: The thermogravimetric analysis was performed using a Mettler Toledo TGA/DSC 1 thermogravimetric analyzer from 30 °C to 600 °C at 20 °C/min under nitrogen atmosphere (60 mL/min). Then the gas is switched to oxygen (60 mL/min) after an isothermal step for 5 minutes and heating up to 800 °C at 20 °C/min. The sample size used was about 5 mg. The degradation onset, degradation maximum, and final degradation temperatures were observed.

DSC: The glass transition temperature (T_g) of the acrylic rubber, acrylonitrile/styrene and polycarbonate regions were determined by a differential scanning calorimeter (DSC). The test was performed by Netzsch F204. The parameter used was: the temperature range was between -120 °C and 180 °C, two times heating and cooling was applied with a rate of 20 °C/min. The nitrogen flow was 70 mL/min. The second heating curve is used for evaluation. The sample weight was about 5 mg.

SEM and EDX: The samples after aging test was examined with SEM Tescan Vega3 XMU (20 kV) and EDS Bruker XFlash 6|30. The coating of the surface was performed by sputtering technique of thin gold-palladium layer before examination.

RESULTS AND DISCUSSION

FT-IR

After the injection molding of the part, the part is cut from the flat surface. The samples are tested for aging up to 1500 h. The samples are taken out for FT-IR measurement for intermediate time intervals of 250 h, 500 h, 750 h, 1000 h, 1250 h, and 1500 h. In Figure 1, the FT-IR measurements are taken from three different regions and on the same position. The absorbance obtained after averaging three measurements were used for calculating the area under the peak. The area change with increasing amount of irradiation has been plotted in terms of carbonyl groups (1728 cm^{-1}) and aromatic groups attached to carbonyl groups (1590 cm^{-1}). In Figure 2, the absorbance area of carbonyl groups after 500 h is increasing till 1250 h and in between 1250 h and 1500 h, the absorbance area increase is slowed down. A similar change was also observed for the aromatic groups attached to carbonyl groups. The photo-oxidation of PC has been initiated by UV and oxygen. Up to 500 h, the PC domains did not degrade significantly which could be due to UV stabilizers. In between 500 h and 1250 h, the degradation was more severe. The degradation reactions are initiated and accelerated by the decreasing amount of UV stabilizers. At this stage, yellow photolytic species namely phenylsalicylates, dihydroxybenzophenones, dihydroxybiphenyl and hydroxydiphenyl ether groups were formed (6–8). Due to the humidity in the aging parameters, the photo-yellowing was also accelerated by the chain-scission mechanism which resulted into lower molecular weight polar polymers; consequently the surface was more vulnerable to erosion through hydrolysis (9). After 1250 h, the surface degradation was slowed down by completion of the active sites in PC degradation species and the penetration of the oxygen into the deeper layers was slowed down. After this stage, the photo-oxidation of PC was reduced by the shielding of the polymer with the formation of dihydroxybenzophenone and yellow species (10).

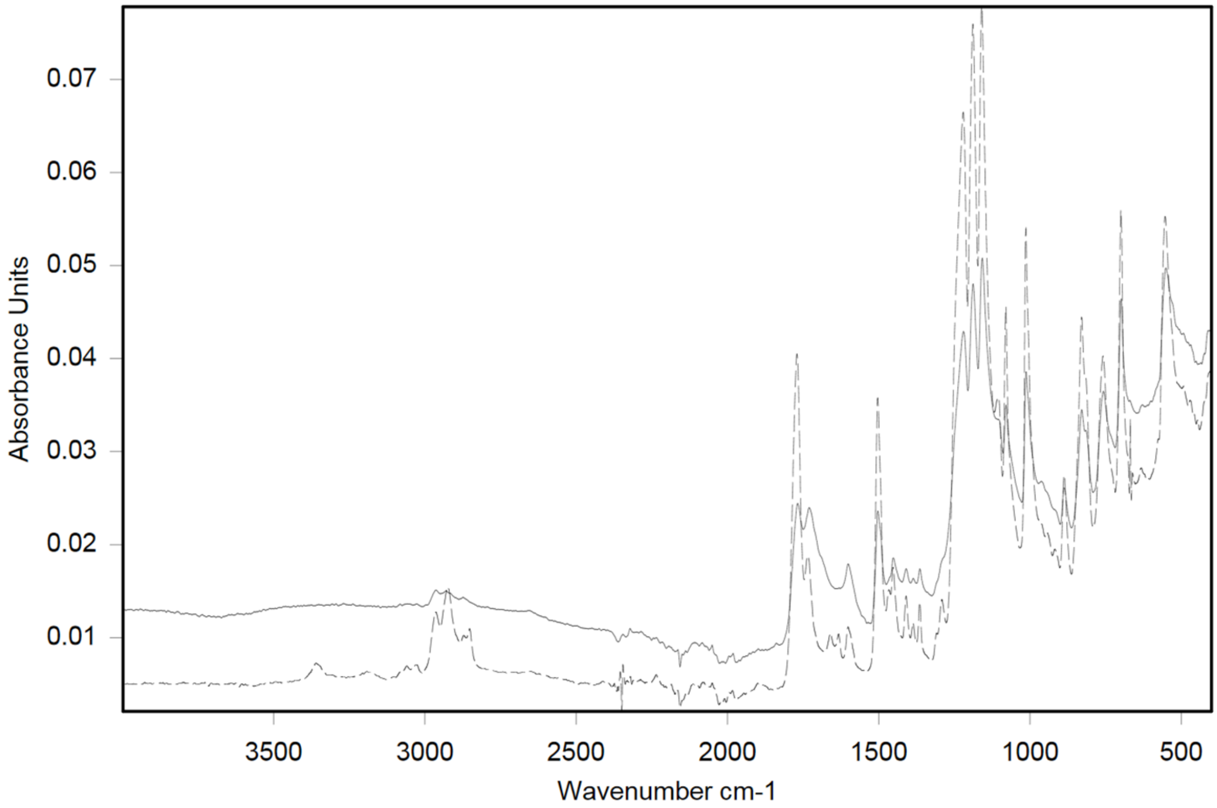


Figure 1: FT-IR ATR spectra of PC/ASA before (--) and after aging 1500 h (—).

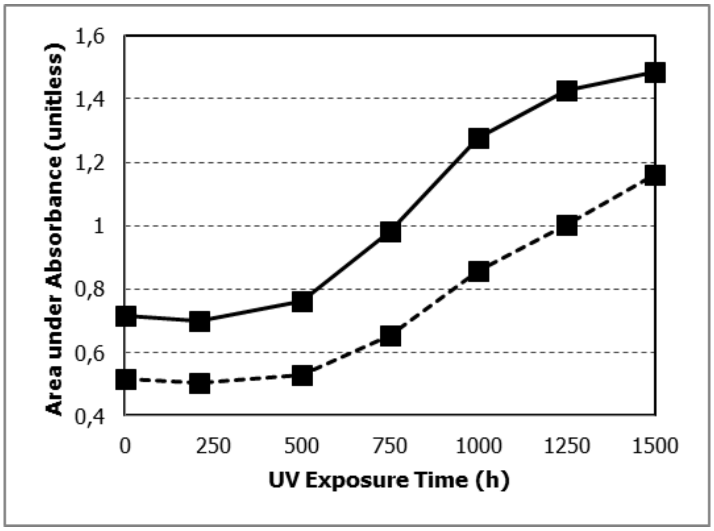


Figure 2: Area under absorbance at carbonyl region (—) and aromatic groups attached to carbonyl groups (--) by UV exposure time.

Spectrophotometry

The color change of the surface was also measured by the same time intervals. In Table 1, the b value referring to the yellowness of the sample is reported. The surface yellowness was increased after 500 h which refers to the formation of yellow degradation species. The increase was not slowed down in between 1250 h and 1500 h referring to the fact that the hydrolysis of degradation products by chain-scission was initiated. It is suggested that after long exposure times, the yellowness index increases where degradation continues by photo-oxidation of photo-Fries products (11). The yellowness of the surface decreased after washing the polar degradation byproducts from the surface.

Table 1: The color change after UV exposure without washing is reported. *The color change after washing the surface.

	0 h	**250 h**	**500 h**	**750 h**	**1000 h**	**1250 h**	**1500 h**	**1500 h***
L	29.13	29.13	29.30	29.97	29.34	30.19	28.79	28.81
a	-0.18	-0.18	-0.23	-0.02	-0.14	-0.21	-0.13	-0.11
b	-0.30	-0.37	-0.34	0.06	0.00	0.80	2.13	0.54

TG/DTG

The TG/DTG curves of PC/ASA before and after aging for 1500 h have been evaluated. In Figure 3, two stages of degradation were observed where the first and second degradation peaks are close to each other. The lower degradation temperature was attributed to the ASA polymers and higher degradation temperature was attributed to the PC polymer in the PC/ASA blend. In Table 2, after the aging the decomposition temperature of both peaks has slightly shifted to the higher temperature. With aging, low molecular mass byproducts have been formed and due to the mobility of the byproducts, the decomposition peak temperature could have shifted to slightly higher temperatures. Since UV degradation has only affected the surface layer and not into the inner layers, the degradation peak temperature did not change drastically.

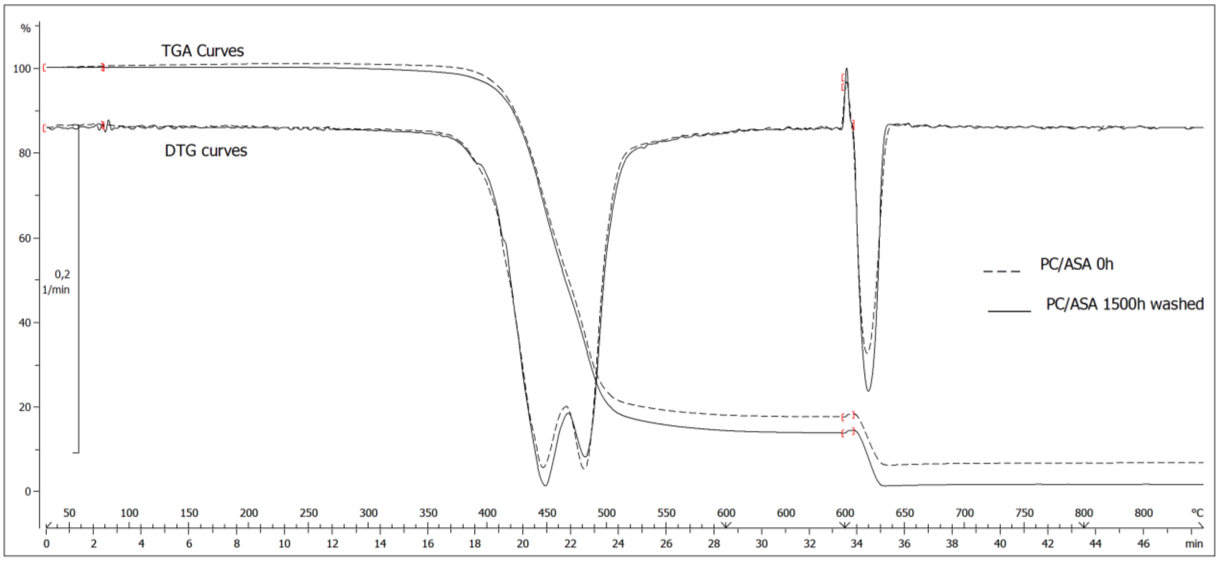


Figure 3: TG/DTG curves representing PC/ASA polymer before aging (--) and 1500 h aging after washed (—).

Table 2: Representative TG/DTG data of PC/ASA polymer before aging and washed after aging.

	TGA Degradation Temperature (°C)		**DTG Degradation Peak Temperature (°C)**	
Sample	**Onset**	**End**	**ASA phase**	**PC phase**
Before	412	495	442	476
After 1500h	413	496	444	477

DSC

The DSC curve has been evaluated before aging and after aging 1500 h (washed) samples. In Figure 4, three glass transition temperatures were detected. The T_g of polycarbonate was at 141≡C, T_g of acrylonitrile/styrene was at 109 °C and T_g of acrylate was about -44 °C. No major change in the T_g was detected which could be attributed that the amorphous polymers PC and SAN phase have not changed the compatibility. The UV exposure did not penetrate to the deeper layers of the sample.

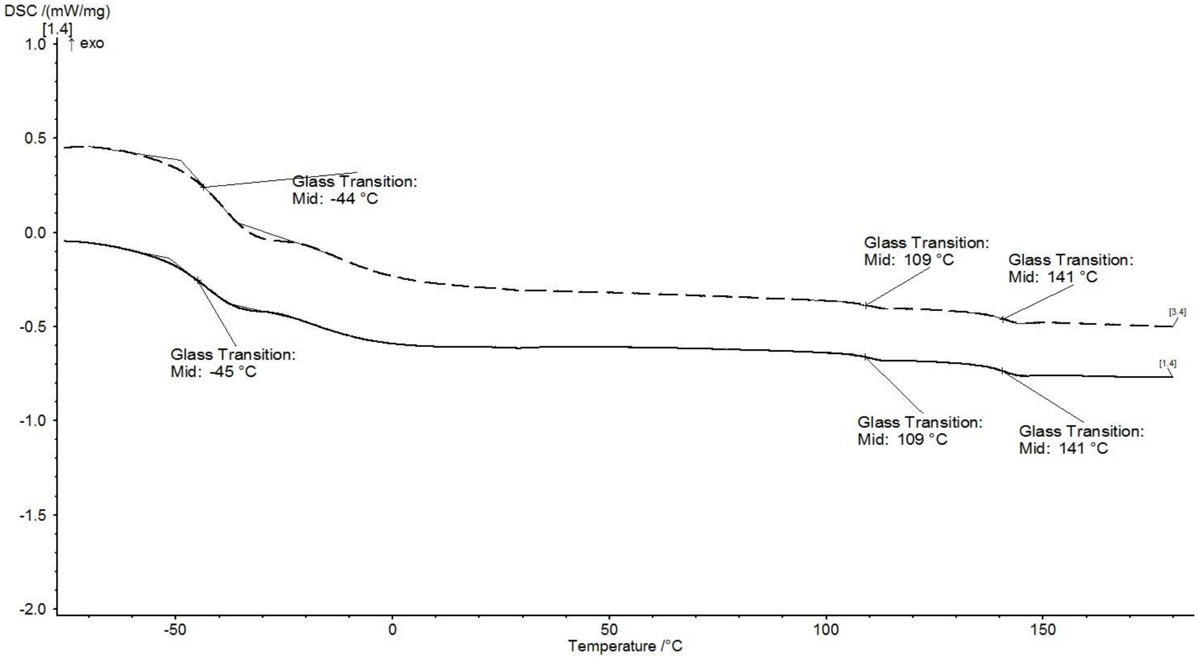


Figure 4: DSC curve representing T_g of PC/ASA polymer before (--) and washed after aging (—).

SEM and EDX

The morphology of the surface after aging was examined by SEM and EDX. The surface of the samples are washed with distilled water and dried with pressurized air. Both the unwashed surface and washed surface have been investigated in order to understand the changes in surface morphology. The unwashed surface after UV radiation for 1500 h was shown in Figure 5. A homogenous distribution of the inorganic fillers which were coming out from the polymer matrix can be observed. Most of the inorganic fillers were more visible meaning that the chemical and physical detachment was almost completed. In Figure 6, after washing the samples with water and dried with pressurized air, the inorganic fillers were diminished meaning that they have been washed out. When the surface morphology of the washed surface was examined, it has been observed that inorganic fillers are embedded into the matrix. As the humidity forms water soluble polar degradation products after chain-scission, the inorganic filler is detached from the matrix by leaving hollow surface. When EDX analysis was performed on the inorganic filler, carbon, oxygen, titanium, zinc and tin was observed (Figure 7). Metal oxides, mainly titanium dioxide, zinc oxide, and tin oxide, could be used as a UV stabilizer or as a pigment in the matrix. Carbon black is the light screening pigment and blocks UV radiation in most of the polymers. On the other hand, fading pigments are used to compensate the color change throughout the UV exposure. Such pigment masks the color changes and stabilizes the color of the polymer. Until 500 h, the color of the polymer surface was shielded by such stabilizers. The inorganic fillers observed in our analysis is therefore could be regarded as the color fading pigment but also UV stabilizer.

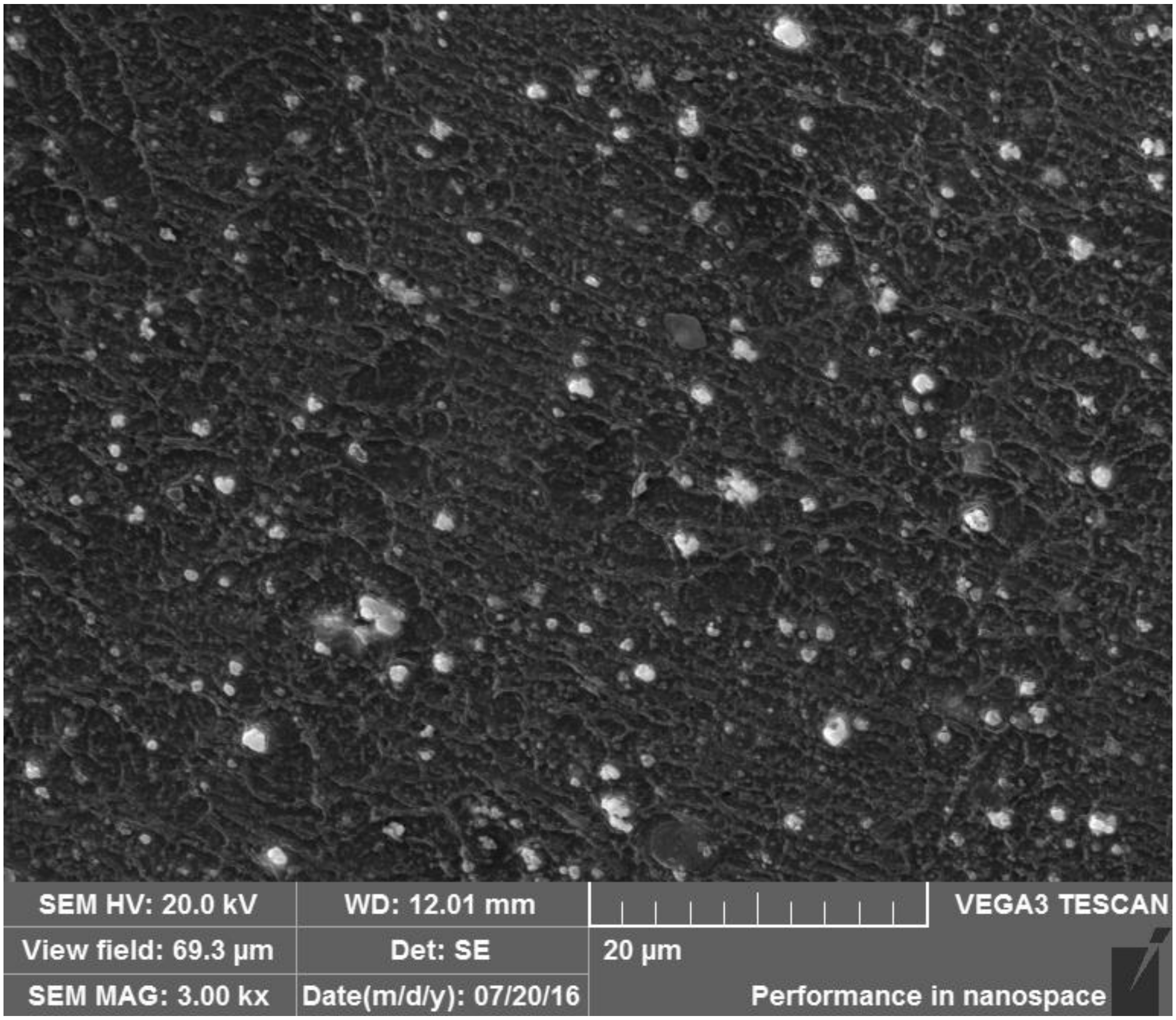
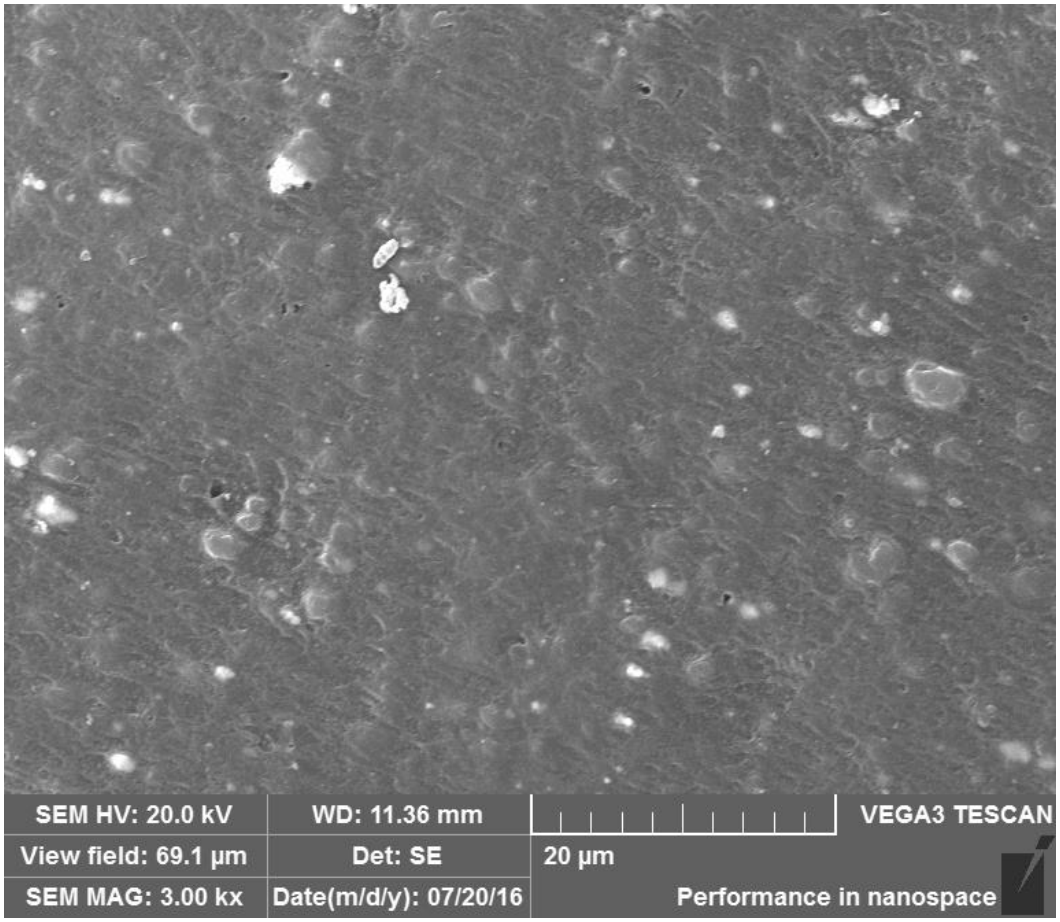


Figure 5: SEM of PC/ASA polymer after aging 1500 h before washing.


SEM HV: 20.0 kV
WD: 11.36 mm
VEGA3 TESCAN
View field: 69.1 μm
Det: SE
20 μm
SEM MAG: 3.00 kx
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Performance in nanospace

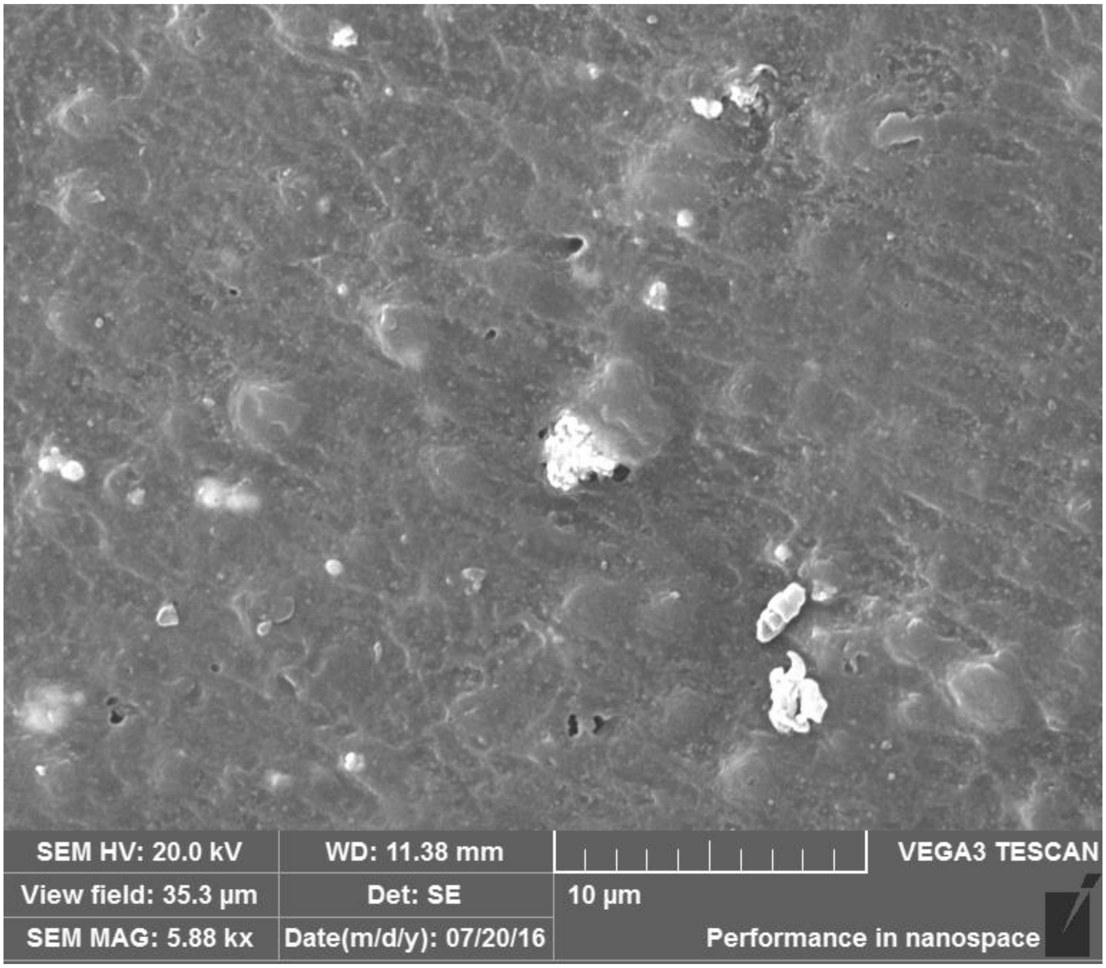

Figure 6: SEM of PC/ASA polymer after aging 1500h (washed surface).

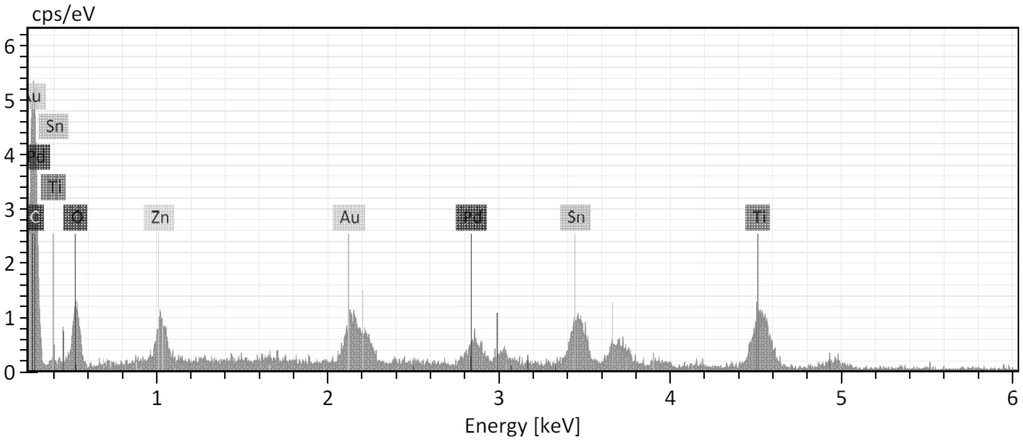

Figure 7: EDX on the inorganic spot of PC/ASA polymer after aging 1500 h (washed surface).

CONCLUSION

As PC/ASA has good chemical, thermal and mechanical properties, the polymer blend could have been chosen for the exterior applications of automotive industry. Since the polymer matrix of PC/ASA has UV stabilizer, the UV exposure performance for 1500 h at a total of 1890 kJ/m^2 was controlled by a weatherometer. The result showed that the degradation of the polycarbonate is accelerated by the UV radiation in the presence of oxygen and humidity. The yellowness of the surface was controlled in time intervals and it has been observed that up to 500 h, the color change is within the control limits. After exposure of sample for 500 h, as the UV radiation degrades the polycarbonate and color fading pigment is detached from the polymer matrix, the UV stabilization effect on the polymer is lost. After 500 h, the predominant UV degradation reactions are photo-Fries rearrangement, photo-oxidation, chain-scission and hydrolysis.

DSC and TGA studies have revealed that no major changes in the thermal properties have occurred. In the FT-IR study, a possible degradation of polycarbonate has been reported in parallel to the previous studies proposed as hydroxyl and carbonyl group formation, chain scission initiated by radicals from the methyl site, recombination reaction, and hydrolysis.

SEM image showed a good dispersion of the inorganic filler. At the end of the aging, most of the inorganic fillers on the surface were able to be washed off by water and pressurized air. The yellowness of the surface has been decreased after washing the water soluble polar degradation byproducts. Nevertheless, still some inorganic filler which were embedded in the structure was visible where others left the surface by leaving hollows on the surface.

In conclusion, PC/ASA developed for application of automotive industry is suitable for interior applications which are not directly exposed to sunlight. On the other hand, it is not applicable to exterior application due to the degradation of PC by UV, oxygen and humidity.

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